

FINAL REPORT

September 1995 to August 1996

NCC2-5142

21-1507-8003

*FINAL
70-25012
OCT.
2002/5/7*

INTERCHANGE FOR JOINT RESEARCH ENTITLED:

**Monitoring of Time-Dependent System Profiles by
Multiplex Gas Chromatography with
Maximum Entropy Demodulation**

Dr. Joseph F. Becker
Professor of Physics
Department of Physics
San Jose State University
San Jose, CA 95192-0106
408-924-5271

Dr. Jose Valentin
Exobiology Branch
Mail Stop 239-12
NASA Ames Research Center
Moffett Field, CA 94035-1000
415-604-5766

The maximum entropy technique was successfully applied to the deconvolution of overlapped chromatographic peaks. An algorithm was written in which the chromatogram was represented as a vector of sample concentrations multiplied by a peak shape matrix. Simulation results demonstrated that there is a trade off between the detector noise and peak resolution in the sense that an increase of the noise level reduced the peak separation that could be recovered by the maximum entropy method. Real data originated from a sample storage column was also deconvoluted using maximum entropy. Deconvolution is useful in this type of system because the conservation of time dependent profiles depends on the band spreading processes in the chromatographic column, which might smooth out the finer details in the concentration profile. The method was also applied to the deconvolution of previously interpreted Pioneer Venus chromatograms. It was found in this case that the correct choice of peak shape function was critical to the sensitivity of maximum entropy in the reconstruction of these chromatograms.

In addition, multiplex gas chromatography was applied for the reconstruction of time varying concentration flows. Using specifically designed input sequences of the sample, a dramatic increase of the time resolution (on the order of at least one order of magnitude) was achieved. When knowledge about the number of compounds present in the sample -- and especially their peak shape functions for the column in use -- was available, the chromatogram was reconstructed from the raw output data by simple linear least squares fitting in most cases. Admittedly, a great amount of pre-information was needed in order to limit the possible set of solutions. However, when pseudo-random binary input sequences were used, the pre-information about the number of compounds could be obtained from the

detector output itself (in most cases). Examples of the monitoring of gases evolving from volcano rock soils and polymers during the heating (from 100°C to 600°C) of these soils by linear temperature programming were reported, as indicated below.

The potential application of multiplex gas chromatography to extraterrestrial atmospheric analysis is quite significant. Contemporary columns and analysis conditions require separation cycle times of about 10 minutes. This means that only very few cycles can be run during the descent of a probe to a planet's surface. Multiplex gas chromatography allows an increase in time resolution through multiple input of the sample during the chromatographic run without having to wait for the completion of one separation cycle to start another. The raw detector output is not directly interpretable since it is the product of overlapping cycles, but we have shown this raw output signal can be demodulated to reconstruct each chromatogram with accuracy.

The results discussed above have been submitted to peer-reviewed journals as listed below:

"Deconvolution of Overlapped Chromatographic Peaks by Maximum Entropy." J.-M. D. Dimandja, M. Kaljurand and J. B. Phillips. *Journal of Chromatography A*. Submitted.

"Non-Stationary Sample Composition Analysis Using Multiple Input Chromatography." J.-M. D. Dimandja, M. Kaljurand and J. R. Valentín. *Analytical Chemistry*. Submitted.